

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 June 2003 (26.06.2003)

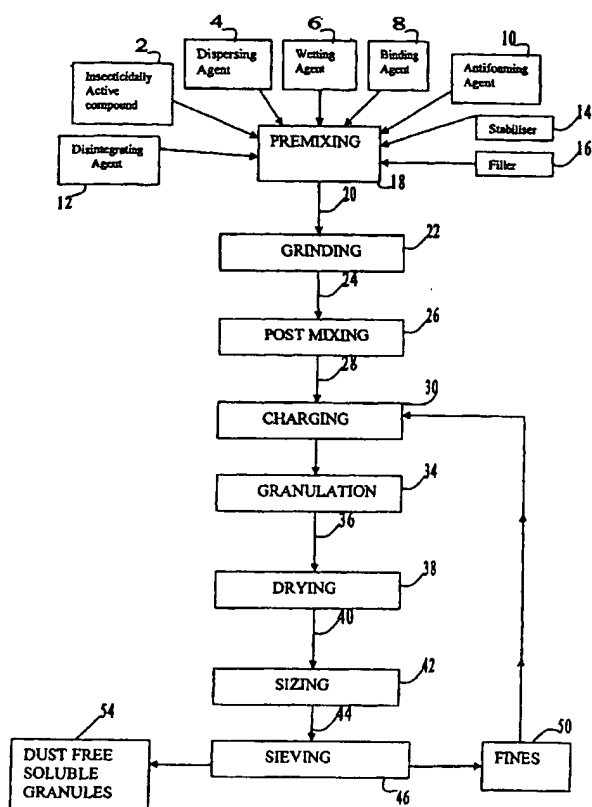
PCT

(10) International Publication Number
WO 03/051606 A1

- (51) International Patent Classification⁷: **B29C 47/00, A01N 25/12**
- (21) International Application Number: **PCT/US02/40353**
- (22) International Filing Date:
18 December 2002 (18.12.2002)
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
60/340,272 18 December 2001 (18.12.2001) **US**
- (71) Applicants: **UNITED PHOSPHORUS, LTD. [IN/IN];** Uniphos House, Madhu Park, 11th Road, Khar (W), Mumbai 400 052 (IN). **UNITED PHOSPHORUS, INC. [US/US];** 423 Riverview Plaza, Trenton, NJ 08611 (US).
- (72) Inventors: **JADHAV, Prakash, Mahadeo;** 12, Hasyvadan Society, Tejpal Scheme, Road No. 4, Vile Parle (East), Mumbai 400 057 (IN). **SHROFF, Rajju Devidas;** 202, Parishram, 40 Pali Hill, Director, Bandra (W), Mumbai 400 057 (IN).
- (74) Agent: **YANCY, Jennifer, P.;** Jones, Tullar & Cooper, P.C., P.O. Box 2266, Eads Station, Arlington, VA 22202 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: A PROCESS FOR PREPARATION OF CHEMICALLY STABLE, DRY-FLOW, LOW COMPACT, DUST FREE, SOLUBLE GRANULES OF PHOSPHOROAMIDOTHIOATES



(57) Abstract: Dry flow, low compact, dust free, soluble granules of phosphoroamidothioates, preferably acephate, are produced by the process of 1) pre-mixing technical grade phosphoroamidothioate with specified adjuvants and other inert ingredients; 2) grinding to produce a ground product having a preferred particle size of 5 microns to 10 microns; 3) postmixing; 4) granulating; 5) drying; 6) sizing to required length, preferably 1.5 to 3.0 mm; 7) and sieving to remove the fines to get the desired dust free soluble granule.

WO 03/051606 A1



(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

A PROCESS FOR PREPARATION OF CHEMICALLY STABLE, DRY-FLOW, LOW
COMPACT, DUST FREE, SOLUBLE GRANULES OF PHOSPHOROAMIDOTHIOATES

CROSS REFERENCE TO RELATED APPLICATION

5 This application claims the benefit, under 35 U.S.C. 119(e), of U.S. Provisional
Application No. 60/340,272 filed December 18, 2001, the contents of which are incorporated
herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

10 The present invention relates to a process for preparing insecticidally active soluble
granules of phosphoroamidothioate, referred to herein as acephate.

2. Background Information

15 In recent years, agricultural chemicals have been most preferably formulated in the
form of dusts, wettable powders, soluble powders, emulsifiable concentrates, soluble liquid/
concentrates, granules, coated granules, water dispersible granules, suspension concentrates,
and solutions. Occasionally, when dusts are produced by absorbing or mixing active
ingredients with a finely divided inert carrier material, for example China Clay or the like,
drift problems occur. With wettable powders and soluble powders the problems faced at the
20 time of dilution are not only drift, but the final disposal of containers, for dust particles tend
to stick to sides of the containers. The left over materials within the containers pose great
problems to the environment, operators and users.

25 Although dusts are undesirable because of airborne contamination and handling
difficulties, liquid spray formulations have not provided an acceptable alternative, for they
involve solvents and packaging expenses, along with container disposal requirements that
detract from their commercial desirability.

30 Water dispersible granules produced by fluidized bed spray dryers overcome the
problems associated with wettable powders and soluble powders, but have high processing
costs and require high value capital investment, as well as requiring highly skilled staff.
These problems impose a significant barrier in widening the market acceptance of these
compounds.

Certain phosphoroamidothioates and phosphoroamidodithioates, collectively referred
to as Phosphoroamidothioates, are known to have excellent insecticidal activity against a

variety of insects and in a variety of environments. Acephate, one of the important commercial insecticides within this class of compounds, is a systemic and contact insecticide of moderate persistence with residual activity lasting about 10-15 days. It is effective against a wide range of aphids, leaf-miners, lepidopterous, larvae, sawflies and thrips and it is also a non-phytotoxic on many crop plants.

Phosphoroamidothioate containing pellets have been proposed in the past, but difficulties have been encountered in pelletizing acephate technical, the preferred insecticide within the class of phosphoroamidothioates. Attempts to manufacture acephate technical pellets from acephate technical powders have been proposed and have been unsuccessful.

Considerable experimentation in the area of producing the preferred high-strength acephate granules has been conducted and confirms the manufacturing difficulties which earlier formulators have experienced. Furthermore, the pellets and methods proposed for making pellets suggested in the prior art leave considerable room for improvement. Prior extrusion processes have proposed the addition of costly surfactants, the combination of phosphoroamidothioate with a second active ingredient, or the creation of a mixture of the active ingredient with a solvent in an amount of from 3-25% by weight before extrusion, but these processes have not solved the problems encountered.

The formulation of acephate presently in use is acephate 75% soluble powder having acephate active ingredient 75% (w/w), surfactant 1 to 2% (w/w), inert filler (precipitated silica) to make 100% (w/w). Acephate 75% soluble powder poses the problems of dust, low pourability, high transportation costs, high capital manufacturing investment, measurement difficulties, difficulties in packing material disposal, handling problems, high risk of caking and others.

Because of the problems associated with producing granular forms of phosphoroamidothioates, such as the preferred acephate, there is a need in the art for a process for preparing chemically stable, dry flow, low compact, dust free, insecticidally active soluble granules of phosphoroamidothioate which are useful from a practical stand point, as well as for a low cost, practical manufacturing technique which can be practiced on a commercial scale without requiring expensive additives or solvents.

SUMMARY OF THE INVENTION.

By the present invention the above-identified major limitations have been overcome. The method for producing dry flow, low-compact, dust free, soluble phosphoroamidothioate

granules, such as the preferred compound acephate, is an improvement over prior manufacturing processes. Further, the dust free soluble granules produced by this invention, which has a concentration of the insecticidally active ingredient in this formulation may vary from 40-98% of phosphoroamidothioate active ingredient, is more advantageous than prior
5 granular products and exhibits certain very desirable characteristics as noted hereinafter.

Briefly, and in accordance with a preferred embodiment of the invention, dry flow, low compact, dust free, soluble granules of insecticidally active phosphoroamidothioate are prepared by forming a pre-mix containing the required quantity of phosphoroamidothioate, a dispersing agent, a wetting agent, a binding agent, an antifoaming agent, a disintegrating
10 agent, a stabilizer and filler. The specified adjuvants have a maximum of 1% water insoluble matter. This pre-mix is then ground to produce a ground product having preferred particle sizes between 5.0 microns to 10.0 microns. The ground product is fed to a post-mixer to form a mixture. The mixture is then fed through a hopper into a granulator where granules are formed. The granules are then dried, and the dried granules are sized and sieved to
15 separate dry granules from fines, producing dry flow, low compact, dust free, soluble granules of phosphoro-amidothioate as noted above, the preferred phosphoroamidothioate is acephate. The fines may be recycled back to the post mixer.

This invention produces essentially dry flow, low compact, dust free soluble phosphoroamidothioate granules having a preferred granule size of 1.5 to 3.0 mm in length
20 and 0.5 to 1.0 mm in diameter. These granules of phosphoroamidothioates are characterized by aging stability for a minimum of two years.

BRIEF DESCRIPTION OF THE DRAWINGS

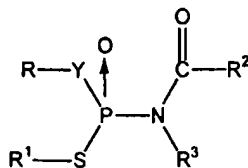
The features and advantages of the present invention will become apparent from the
25 following detailed description of preferred embodiments thereof, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a flow chart of the preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 The process of the present invention is best described by referring to the flow chart in FIG. 1. An essentially dry pre-mix comprising about 95% to 99% of solids and 1% to 5% moisture and/or solvent is formed from the following ingredients: 40% to 98% of the insecticidally active compound 2, 0.1% to 5.0% dispersing agent 4, 0.1% to 3.0% wetting

agent **6**, 0.1% to 3.0% binding agent **8**, 0.01% to 0.08% antifoaming agent **10**, 0.01% to 10.0% disintegrating agent **12**, 0.01% to 1.0% stabilizer **14**, and fillers **16** to make 100% (w/w). The insecticidally active compounds of the present invention have the following formula:



wherein R and R¹ individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group contains 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R³ is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur. All of the inert ingredients are preferably solids and in a powder form. In one preferred embodiment, the binding agent 8 is selected from sucrose and starch derivatives or a blend thereof, the wetting agent 6 is selected from calcium or sodium salt of alkyl aryl sulphonate, the dispersing agent 4 is selected from the derivative of sulfonated fatty alcohols, the disintegrating agent 12 is selected from swelling type clays such as Bentonite and zeolite, the antifoaming agent 10 is selected from silicon oil derivatives, the stabiliser 14 is selected from salts of higher fatty acids, and the filler 16 is selected from precipitated silica and kaoline and the like. Grinding 22 of the pre-mix 20 is then conducted, preferably in a microniser, to obtain a ground product 24 having a preferred particle size of 5 microns to 10 microns.

20 The ground product 24 is subjected to post-mixing 26 to form a mixture 28 which is then made into granules 36 by preferably charging 30, by way of a rotary feeder, a feeding hopper which supplies the mixture to a granulator for granulation 34. The granulator that performs the granulation 34 has a preferred inlet temperature between 30 to 35°C and a preferred outlet temperature of between 40°C to 45°C. The resulting granules 36 are
25 subjected to a drying 38 process, preferably by passing the granules 36 through an air chamber, producing dry granules 40.

Sizing 42 the dry granules 40 is then accomplished to produce sized granules 44 of a desired length and diameter. Sizing the granules is preferably conducted by passing the dry granules 40 through an oscillating cutter to obtain granules which are preferably between

about 1.5 mm and 3.0 mm in length and 0.5 mm to 1.0 mm in diameter. After sizing, the sized granules 44 are subjected to sieving 46 to separate fines 50 generated during the sizing process from desired dust free soluble granules 51.

The fines 50 from the sieving 46 process may be collected and recycled at the charging 30 stage of the process to obtain a minimum yield of 99.0% dry flowable, low compact, dust free, soluble granules 54 of phosphoroamidothioates, preferably acephate.

The dust free soluble granules 54 were tested for required quality specifications and packed in desired packing. This technique gives 99% of conversion yield. The dust free soluble granules 54 enjoy all the formulation advantages described above, producing dust free soluble granules 54 which are beneficial from an economic aspect and a handling aspect and which show a very good performance during use.

The following examples are presented to illustrate but not to restrict the present invention. Parts and percentage are by weight unless otherwise specified.

EXAMPLE 1

15 Acephate 97% Granules can be prepared as follows:

Composition

	<u>Ingredients</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	98.48
	Dispersing agent	0.50
20	Wetting agent	0.10
	Binding agent	0.10
	Antifoaming agent	0.03
	Disintegrating agent	0.50
	Stabilizer	0.05
25	Filler	0.24

	Total ...	100.00

EXAMPLE 1 PROCESS:

The constituents of the above composition are mixed in a pre-mixer, then ground in a microniser to the required size of 5 micron to 10 micron. The ground product 24 is again mixed in a post-mixer to get a uniform homogeneous mixture 28. This homogeneous mixture 28 is then fed through a rotary feeder into a low compaction granulator, while maintaining an inlet temperature of 32 to 35°C and an outlet temperature of 40 to 45°C. The Acephate

granules 36 formed in the granulator are further dried through an air chamber, sized to 1.5 mm to 3 mm length, and are collected. The fines 50 generated during the process are recharged to get a conversion yield of 99 percent.

EXAMPLE 2

5 Acephate 98% granules can be prepared as follows:

Composition

	<u>Ingredient</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	99.50
	Dispersing agent	0.25
10	Wetting agent	0.03
	Binding agent	0.05
	Antifoaming agent	0.02
	Disintegrating agent	0.05
	Stabilizer	0.05
15	Filler	<u>0.05</u>
	Total	100.00

Acephate 98% granules with above composition can be prepared by following the process described in EXAMPLE 1.

20

EXAMPLE 3

Acephate 97.5% granules can be prepared as follows:

Composition

	<u>Ingredient</u>	<u>Quantity (% w/w)</u>
25	Acephate Technical 98.5% purity	98.99
	Dispersing agent	0.40
	Wetting agent	0.10
	Binding agent	0.10
	Antifoaming agent	0.03
30	Disintegrating agent	0.20
	Stabilizer	0.05
	Filler	<u>0.13</u>
	Total	100.00

Acephate 97.5% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 4

5 Acephate 90% Granules can be prepared as follows:

Composition

	<u>Ingredient</u>	<u>Quantity(% w/w)</u>
	Acephate Technical 98.5% purity	91.38
	Dispersing agent	00.75
10	Wetting agent	00.10
	Binding agent	00.20
	Antifoaming agent	00.03
	Disintegrating agent	01.00
	Stabilizer	00.50
15	Filler	06.04

	Total ...	100.00

Acephate 90% granules with above composition can be prepared by following the process described in EXAMPLE 1.

20

EXAMPLE 5

Acephate 85% granules can be prepared as follows:

Composition

	<u>Ingredient</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	86.30
25	Dispersing agent	01.50
	Wetting agent	00.50
	Binding agent	01.00
	Antifoamer	00.05
	Disintegrating agent	02.00
30	Stabilizer	00.60
	Filler	08.05

	Total ...	100.00

Acephate 85% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 6

Acephate 75% Granules can be prepared as follows:

5 Composition

	<u>Ingredient</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	76.15
	Dispersing agent	2.00
	Wetting agent	1.50
10	Binding agent	1.50
	Antifoaming agent	0.06
	Disintegrating agent	5.00
	Stabilizer	0.75
	Filler	13.04
15		-----
	Total ...	100.00

Acephate 75% Granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 7

20 Acephate 50% Granules can be prepared as follows:

Composition

	<u>Ingredients</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	50.77
	Dispersing agent	3.00
25	Wetting agent	2.00
	Binding agent	3.00
	Antifoaming agent	0.08
	Disintegrating agent	10.00
	Stabilizer	1.00
30	Filler	30.15

	Total ...	100.00

Acephate 50% Granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 8

5 Acephate 40% granules can be prepared as follows:

Composition

	<u>Ingredient</u>	<u>Quantity (% w/w)</u>
	Acephate Technical 98.5% purity	40.61
	Dispersing agent	4.50
10	Wetting agent	3.00
	Binding agent	3.00
	Antifoaming agent	0.08
	Disintegrating agent	12.00
	Stabilizer	1.50
15	Filler	<u>35.31</u>
	Total	100.00

Acephate 40% Granules of above composition can be prepared by following the process described in EXAMPLE 1.

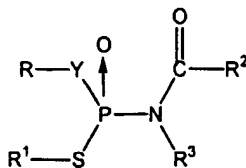
TESTS:

20 The physical properties of Acephate granules were determined before and after aging at 45°C for 500 hrs and for flowability, wetting time, attrition test, disintegration rate, tap density, suspensibility, sedimentation and persistent foam. No noticeable difference in all the above properties was observed. The dynamic wetting time and solubility test was measured as per MT-167 of CIPAC. The flowability was measured as per MT-172 of CIPAC. The dry
25 sieve analysis was measured as per MT-170 of CIPAC. The sedimentation was measured as per MT-15.1 of CIPAC. Dustiness of granules was measured as per MT-171 of CIPAC. The tap density was measured as per MT-58.4 and MT-33 of CIPAC. The Acephate technical was determined by the GLC method published in AOAC.

30 Although the present invention has been disclosed in terms of a preferred embodiment, it will be understood that numerous additional modifications and variations can be made without departing from the scope of the invention as defined by the following claims.

What is claimed is:

1. A process for preparing soluble granules comprising
- a) premixing 40 to 98 wt.% an insecticidally active compound of the following
- a:



wherein R and R¹ individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R³ is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur;

0.1-5.0 wt.% a dispersing agent; 0.1-3.0 wt.% a wetting agent; 0.1-3.0 wt.% a binding agent; 0.01-0.08 wt.% an antifoaming agent; 0.01-10.0 wt.% a disintegrating agent; 0.01-1.0 wt.% a stabilizer; and fillers to make 100 wt.%, to form a premix comprising essentially 95-99% solids and 1-5% moisture and/or solids;

- 15 b) grinding said premix to produce a ground product having a predetermined particle size;
- c) post-mixing said ground product to produce a mixture;
- d) granulating said mixture to produce granules;
- e) drying said granules to produce dry granules;
- 20 f) sizing said dry granules to produce sized granules having a predetermined length and a predetermined diameter; and
- g) sieving said sized granules to separate fines which are less than said predetermined length and said predetermined diameter.

- 25 2. The process of claim 1, wherein said ground product has a predetermined particle size of 5-10 microns.

3. The process of claim 1, wherein said dry granules have a predetermined length of 1.5-3.0 mm.

4. The process of claim 1, wherein said dry granules have a predetermined diameter of 0.5 to 1.0 mm.

5. The process claimed in claim 1, wherein said fillers are solids in powder form.

5

6. The process of claim 1, wherein said binding agent is a blend of sucrose and starch derivatives.

7. The process of claim 1, wherein said wetting agent is selected from the group comprising calcium salt of alkyl aryl sulphonate and sodium salt of alkyl aryl sulphonate.

10

8. The process of claim 1, wherein said dispersing agent is a derivative of sulfonated fatty alcohol.

9. The process of claim 1, wherein said disintegrating agent is a swelling type clay selected from the group comprising bentonite and zeolite.

15

10. The process of claim 1, wherein said antifoaming agent is silicon oil derivative.

11. The process of claim 1, wherein said stabilizer is a salt of a higher fatty acid.

20

12. The process of claim 1, wherein said fillers are selected from the group comprising precipitated silica and kaoline.

13. The process of claim 1, wherein said granulation is accomplished by passing said mixture through an orifice having an inlet and an outlet.

25

14. The process of claim 13, wherein said inlet has a temperature of 30-35 °C.

15. The process of claim 13, wherein said outlet has a temperature of 40-45°C.

30

16. The process of claim 1, wherein said drying is accomplished by passing said granules through an air chamber.

17. The process of claim 1, wherein said grinding is accomplished by a microniser.
18. The process of claim 1, wherein said sizing is accomplished by an oscillating
5 cutter.
19. The process of claim 1, wherein said insecticidally active compound is acephate.
20. The process of claim 1, further comprising;
10 h) recycling said fines into step d).
21. The process of claim 20, wherein said insecticidally active compound is acephate.
22. The process of claim 21, wherein said ground product has a predetermined
15 particle size of 5-10 microns.
23. The process of claim 22, wherein said dry granules have a predetermined length
of 1.5-3.0 mm and a predetermined diameter of 0.5 to 1.0 mm.
- 20 24. The process of claim 23, wherein said binding agent is a blend of sucrose and
starch derivatives.
25. The process of claim 24, wherein said wetting agent is selected from the group
comprising calcium salt of alkyl aryl sulphonate and sodium salt of alkyl aryl sulphonate.
25
26. The process of claim 25, wherein said dispersing agent is a derivative of
sulfonated fatty alcohol.
27. The process of claim 26, wherein said disintegrating agent is a swelling type clay
30 selected from the group comprising bentonite and zeolite.
28. The process of claim 27, wherein said antifoaming agent is silicon oil derivative.

29. The process of claim 28, wherein said stabilizer is a salt of a higher fatty acid.

30. The process of claim 29, wherein said fillers are selected from the group comprising precipitated silica and kaoline.

5

31. The process of claim 20, wherein said granulation is accomplished by passing said mixture through an orifice having an inlet and an outlet.

32. The process of claim 31, wherein said inlet has a temperature of 30-35 °C and said outlet has a temperature of 40-45°C.

10

33. The process of claim 32, wherein said drying is accomplished by passing said granules through an air chamber.

15

34. The process of claim 33, wherein said grinding is accomplished by a microniser.

35. The process of claim 34, wherein said sizing is accomplished by an oscillating cutter.

20

36. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 1.

37. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 5.

25

38. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 19.

39. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 20.

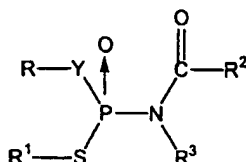
30

40. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 21.

41. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 30.

5 42. A process for preparing soluble granules comprising

a) preparing a dry premix by premixing 40 to 98 wt.% an insecticidally active compound of the following formula:



10 wherein R and R¹ individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R³ is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur;

0.1-3.0 wt. % a wetting agent and a filler to make 100 wt.%;

15 b) grinding said dry premix to produce a ground product having a predetermined particle size;

c) post-mixing said ground product to produce a mixture;

d) granulating said mixture to produce granules;

e) drying said granules to produce dry granules;

20 f) sizing said dry granules to produce granules having a predetermined length and a predetermined diameter; and

g) sieving said sized granules to separate fines which are less than said predetermined length and said predetermined diameter.

25 43. The process of claim 42, wherein said wetting agent is selected from the group comprising calcium salt of alkyl aryl sulphonate and sodium salt of alkyl aryl sulphonate.

44. The process of claim 42, wherein said filler is selected from the group comprising precipitated silica and kaoline.

30

45. The process of claim 44, wherein said wetting agent is selected from the group comprising calcium salt of alkyl aryl sulphonate and sodium salt of alkyl aryl sulphonate.

46. The process of claim 42, wherein said step of preparing said dry premix further
5 comprises premixing 0.1-5.0 wt.% a dispersing agent.

47. The process of claim 46, wherein said dispersing agent is a derivative of sulfonated fatty alcohol.

10 48. The process of claim 42, wherein said step of preparing said dry premix further comprises premixing 0.1-3.0 wt. % a binding agent.

49. The process of claim 48, wherein said binding agent is a blend of sucrose and starch derivatives.

15 50. The process of claim 42, wherein said step of preparing said dry premix further comprises premixing 0.01-0.08 wt.% an antifoaming agent.

20 51. The process of claim 50, wherein said antifoaming agent is a silicon oil derivative.

52. The process of claim 42, wherein said step of preparing said dry premix further comprises premixing 0.01-10 wt.% a disintegrating agent.

25 53. The process of claim 52, wherein said disintegrating agent is a swelling type clay selected from the group comprising bentonite and zeolite.

54. The process of claim 42, wherein said step of preparing said dry premix further comprises premixing 0.01-1.0 wt.% a stabilizer.

30 55. The process of claim 54, wherein said stabilizer is a salt of a higher fatty acid.

56. The process of claim 42, wherein said insecticidally active compound is acephate.

57. The process of claim 42, further comprising;

h) recycling said fines into step d).

58. The process of claim 57, wherein said insecticidally active compound is acephate.

5

59. The process of claim 42, wherein said dry premix is substantially free from water or solvent.

60. The process of claim 42, wherein said step of preparing said dry premix further
10 comprises premixing 0.1-5.0 wt.% a dispersing agent, 0.1-3.0 wt.% a binding agent, 0.01-0.08 wt.% an antifoaming agent, 0.01-10 wt.% a disintegrating agent, 0.01-1.0 wt.% a stabilizer.

61. The process of claim 60, wherein said insecticidally active compound is acephate.

15

62. The process of claim 61, wherein said dispersing agent is a derivative of sulfonated fatty alcohol, said binding agent is a blend of sucrose and starch derivatives, said antifoaming agent is a silicon oil derivative, said disintegrating agent is selected from the group comprising bentonite and zeolite, and said stabilizer is a salt of a higher fatty acid.

20

63. The process of claim 62, wherein said dry premix is substantially free of water or solvent.

64. The process of claim 60, wherein said dry premix is substantially free of water or
25 solvent.

65. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 42.

30 66. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 43.

67. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 44.

68. A chemically stable phosphoroamidothioate granule prepared by a process
5 comprising the steps of claim 45.

69. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 46.

10 70. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 48.

71. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 50.
15

72. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 52.

73. A chemically stable phosphoroamidothioate granule prepared by a process
20 comprising the steps of claim 54.

74. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 56.

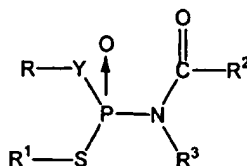
25 75. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 57.

76. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 58.
30

77. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 59.

78. A process for preparing soluble granules consisting essentially,

a) preparing a dry premix by premixing 40 to 98 wt.% an insecticidally active compound of the following formula:



5 wherein R and R¹ individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R² is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R³ is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur;

10 0.1-5.0 wt.% a dispersing agent; 0.1-3.0 wt. % a wetting agent; 0.1-3.0 wt.% a binding agent; 0.01-0.08 wt.% an antifoaming agent; 0.01-10.0 wt.% a disintegrating agent; 0.01-1.0 wt.% a stabilizer; and a filler to make 100 wt.% ;

b) grinding said dry premix to produce a ground product having a predetermined particle size;

15 c) post-mixing said ground product to produce a mixture;

d) granulating said mixture to produce granules;

e) drying said granules to produce dry granules;

f) sizing said dry granules to produce granules having a predetermined length and a predetermined diameter; and

20 g) sieving said sized granules to separate fines which are less than said predetermined length and said predetermined diameter.

79. The process of claim 78, wherein said binding agent is a blend of sucrose and starch derivatives.

25

80. The process of claim 78, wherein said wetting agent is selected from the group comprising calcium salt of alkyl aryl sulphonate and sodium salt of alkyl aryl sulphonate.

81. The process of claim 78, wherein said dispersing agent is a derivative of
30 sulfonated fatty alcohol.

82. The process of claim 78, wherein said disintegrating agent is a swelling type clay selected from the group comprising bentonite and zeolite.

5 83. The process of claim 78, wherein said antifoaming agent is silicon oil derivative.

84. The process of claim 78, wherein said stabilizer is a salt of a higher fatty acid.

85. The process of claim 78, wherein said filler is selected from the group comprising
10 precipitated silica and kaoline.

86. The process of claim 78, wherein said insecticidally active compound is acephate.

87. The process of claim 78, wherein said dry premix is substantially free of water or
15 solvent.

88. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 78.

20 89. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 86.

90. A chemically stable phosphoroamidothioate granule prepared by a process comprising the steps of claim 87.

25

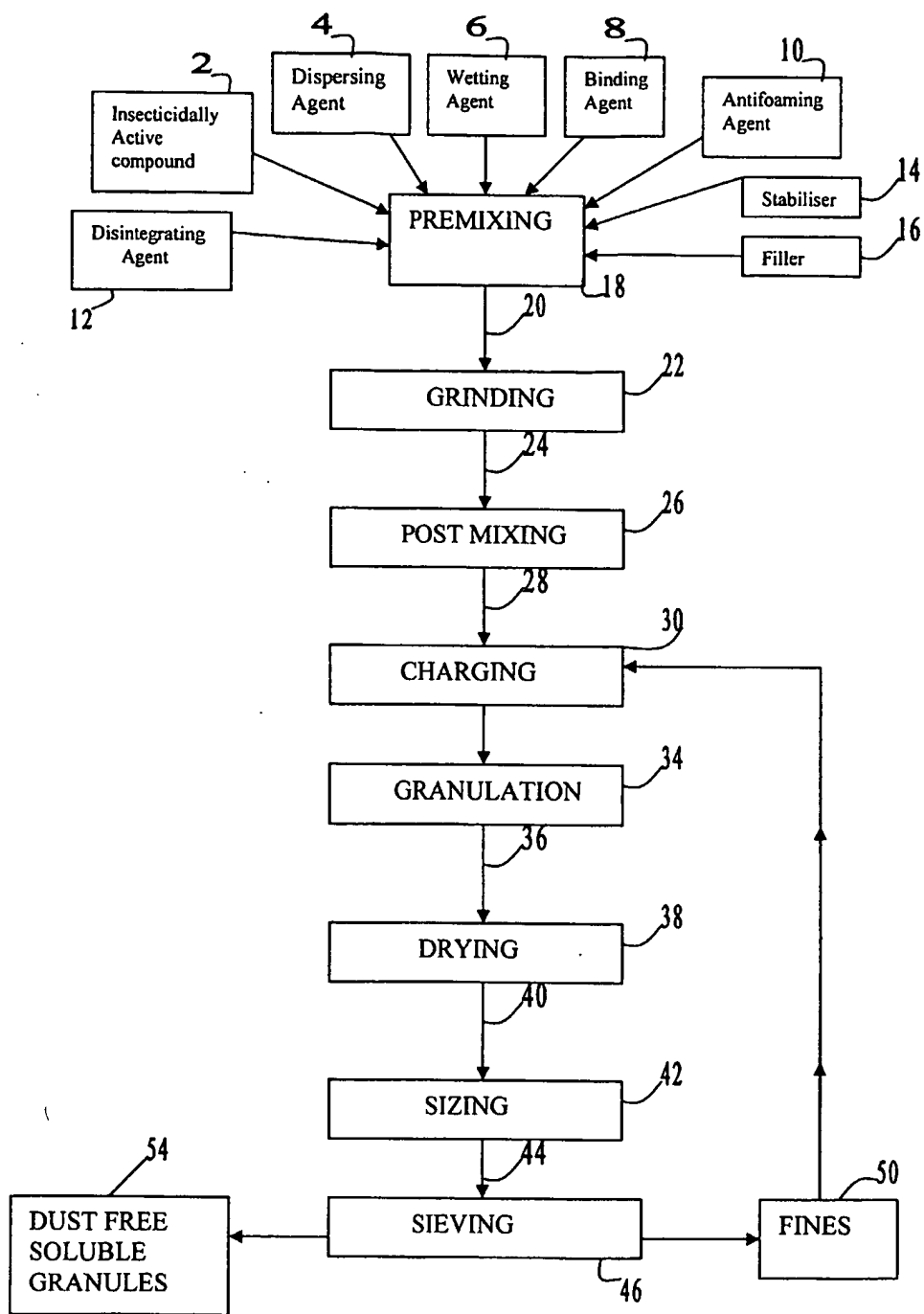


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/40353

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B29C 47/00; A01N 25/12
US CL : 264/142, 211; 424408; 514/120

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 264/142, 211; 424408; 514/120

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,544,553 A (SMOLANOFF et al) 01 October 1985, 01.10.1985), see entire document.	1-90
Y	US 5,650,163 A (CANNELONGO) 22 July 1997 (22.07.1997), see entire document.	1-90
Y	WO 98/26656 (TOMEN ARGO, INC.) 25 June 1998 (25.06.1998), see entire document.	1-90

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

21 March 2003 (21.03.2003)

Date of mailing of the international search report

22 APR 2003

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Mark Eashoo, Ph.D.

Telephone No. (703) 308-0661

Jean Proulx
Paralegal